University of Technology, Sydney
Faculty of Science
Department of Chemistry and Forensic Science

INVESTIGATION OF MAGNESIA REACTIVITY IN BLENDED CEMENT SYSTEMS UNDER HYDROTHERMAL CONDITIONS

by
Barry Liu

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Certificate of Authorship / Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in this thesis.

Barry Liu

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Abstract

Addition of supplementary cementing materials (SCM) to produce blended Portland cements (PC) is a well established practice in the manufacture of construction materials. It enables an overall reduction in the consumption of PC thereby reducing CO_2 emissions. This study reports findings on the hydrothermal chemistry, physical and mechanical properties of autoclaved PC–quartz blends where PC was partially replaced by reactive magnesia (MgO), which requires less energy for calcination than calcia (CaO) from their naturally occurring carbonates, and alumina-silica rich fired clay-brick (CB) waste fines, an abundant industrial waste and a proven SCM.

The dependence of the reactivity of magnesia on the calcination temperature was initially investigated through the hydration behaviour and an optimum reactivity at a temperature of 600°C was identified. In order to investigate the potential of this reactive magnesia in a cement environment, the reactivity of the magnesia with colloidal silica in model $MgO\text{-}SiO_2\text{-}H_2O$ slurry systems was first investigated under both 'mild' and 'extreme' hydrothermal reaction conditions. Amorphous magnesium silicate hydrate (M-S-H) phases were identified in the 'mild' conditions at 180°C with increasingly crystalline phases being developed as the temperature and time were increased up to 350°C and 16 hours of hydrothermal treatment. Two different reaction sequences were also established. For M/S ratios of 0.6, 0.8 and 1.0, the principal reaction products were M-S-H gel and talc while for M/S ratios of 1.5 and 2.0, they were brucite, deweylite and chrysotile serpentine. Morphological studies using SEM of the specimens containing chrysotile revealed that the chrysotile was not of a fibrous nature.

The addition of reactive MgO to PC in hydrothermal conditions was observed to have a negative effect on the compressive strength. The only magnesium containing phase observed in XRD was brucite, indicating that MgO did not take part in the reaction during the hydration of the cement. No M-S-H phases were observed in the MgO containing mixes. Experimental results suggested that MgO was not entirely inert as the formation of tobermorite appeared to be retarded in the presence of brucite.

Examination of PC-quartz mortar mixes revealed that alumina-silica rich clay-brick waste is pozzolanic where the Al_2O_3 provided a source of Al ions for the accelerated formation of Al substituted 1.1nm tobermorite. Mechanical properties showed

improvements with the incorporation of CB waste in more silica-rich environments. Moreover, drying shrinkage and resistance to carbonation were improved due to increased crystallinity of Al-tobermorite.

For blended PC with the addition of both CB waste and reactive magnesia (in a 50/50 ratio), an apparent synergy was observed as minimal (or no) reduction in strength was observed for up to 20% additions of the 50/50 blend. The synergy was explained by the contrasting physical and chemical effects as a result of attaining an optimum proportion of amorphous and crystalline material and optimum physical packing conditions.

Autoclaved MgO-SiO_2 only cube specimens were shown to be capable of producing strength up to 10MPa. XRD revealed the presence of talc where the talc crystallinity was higher in the MgO-silica fume specimens which corresponded to higher strength specimens. This has the potential to be used for low strength applications such as interior walls, possibly as a replacement for gypsum plasterboards.

The use of fired clay-brick waste in combination with reactive magnesia as additives for the production of hydrothermally cured cement-based building products has the potential to achieve an overall positive outcome from an environmental viewpoint.

Table of Contents

List of Publications by the Author

1. B. Liu, A. Ray, and P.S. Thomas (2008). "Physical and mechanical properties of autoclaved alumina-silica rich industrial waste cement systems incorporating reactive magnesia." Concrete Forum 1(1): 18-22.

2. B. Liu, A. Ray, and P.S. Thomas (2007). "Autoclaved alumina-silica rich industrial waste cement systems incorporating magnesia." International Congress on the Chemistry of Cement, Montreal, Canada.

3. B. Liu, A. Ray, and P.S. Thomas (2007). "Strength development in autoclaved aluminosilicate rich industrial waste-cement systems containing reactive magnesia." Journal of the Australian Ceramic Society 43(1): 82-87.

4. B. Liu, P.S. Thomas, A.S. Ray, and J.P. Guerbois (2007). "A TG Analysis of the Effect of Calcination Conditions on the Properties of Reactive Magnesia." Journal of Thermal Analysis and Calorimetry 88(1): 145-149.

5. B. Liu, A. Ray, P.S. Thomas, D. Klimesch and J.P. Guerbois (2007). "Mechanical properties of hydrothermally treated alumina-silica rich industrial waste cement systems - effect of magnesia addition." Journal of Solid Waste Technology and Management 33(2): 61-66.

List of Abbreviations

AAC	Autoclaved Aerated Concrete
AFm	Al_2O_3-Fe_2O_3-mono phase, $[Ca_2(Al,Fe)(OH)_6]\cdot X\cdot xH_2O$, X = one formula unit of a singly charged anion, or half a formula unit of a doubly charged anion.
(Al)-C-S-H	Al substituted C-S-H
AIR	Acid Insoluble Residue
ASTM	American Society for Testing and Materials
ATH	Aluminium Trihydrate
C_2S	Dicalcium Silicate
C_2SH	Dicalcium Silicate Hydrate
C_3A	Tricalcium Aluminate
C_3AH_6	Hydrogarnet
C_3ASH_4	Katoite
C_3AS_3	Grossular
C_3S	Tricalcium Silicate
C_4AF	Tetracalcium Aluminoferrite
C_6S_6H	Xonotlite
CB	Clay-Brick
CH	Calcium Hydroxide (Portlandite)
CS	Wollastonite
C-S-H	Calcium Silicate Hydrate
DDT	2nd Derivative Differential Thermal
DoC	Degree of Carbonation
DTA	Differential Thermal Analysis
EGA	Evolved Gas Analysis
ESEM	Environmental Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
FID	Free-Induction Decay
FT	Fourier Transform
GGBFS	Ground Granulated Blast-Furnace Slag
ICCD	International Centre for Diffraction Data
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
LOI	Loss on Ignition
M/S	MgO/SiO_2 Ratio
M-A-S-H	Magnesium Aluminium Silicate Hydrate
M-S-H	Magnesium Silicate Hydrate
MAS	Magic Angle Spinning
MK	Metakaolin
MPa	Megapascal

NMR	Nuclear Magnetic Resonance
OPC	Ordinary Portland Cement
PC	Portland Cement
PFA	Pulverised Fuel Ash
ppm	Parts Per Million
PSA	Particle Size Analyses
RH	Relative Humidity
SCM	Supplementary Cementing Materials
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
TMS	Trimethylsilylation
WDS	Wavelength Dispersive Spectrometry
w/c	Water/Cement Ratio
w/s	Water/Solid Ratio
wt.%	Weight Percent
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

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